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PIC (Products of Incomplete Combustion) Formation under Pyrolytic and Starved Air Conditions

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PIC FORMATION UNDER PYROLYTIC AND STARVED AIR CONDITIONS

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A comprehensive program of laboratory studies based on the non-flame mode of thermal decomposition produced much data on PIC (Products of Incomplete Combustion) formation, primarily under pyrolytic and starved air conditions.

Most significantly, laboratory results from non-flame studies were compared to those from various field tests to evaluate incinerability relationships. Measurement of gas-phase thermal stability in an atmosphere of low oxygen concentration yielded results of incinerability ranking that were far more consistent with the findings from field tests than any one of several common methods applied in the past such as those that employed heat of combustion, autoignition temperature, etc.

The results of four experimental studies were presented as significant contributions to developing/expanding the data base on POHC (Principal Organic Hazardous Constituent) stability and PIC formation for pure compounds and mixtures.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes the results of various laboratory studies designed to correlate predictions based on laboratory findings to field results, with emphasis on Products of Incomplete Combustion (PIC) formation under pyrolytic and starved air conditions in the laboratory tests.

For further information, please contact the Alternative Technologies Division/Thermal Destruction Branch of the Hazardous Waste Engineering Research Laboratory.

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ABSTRACT

The University of Dayton Research Institute carried out a comprehensive program of laboratory studies based on the non-flame mode of hazardous waste thermal decomposition. The results of those studies were compared to those of flame-mode studies and of field tests to evaluate the incineration model proposed. That model was developed upon the premise that incinerators do not operate continuously at optimum conditions. As a result, as much, or more, than one percent of the feed and its flame treatment products must undergo further decomposition in the post-flame region to meet the >99.99% Destruction and Removal Efficiency (DRE) criterion.

Thermal decomposition (non-flame) results were compared to those from a flame-mode study. That comparison supported a common order of stability ranking of individual compounds set forth by the findings from both series.

Laboratory results from non-flame studies were compared to those from various field tests to evaluate incinerability relationships. It was strongly evident that the results of the laboratory tests where low oxygen conditions (gas-phase thermal stability at low oxygen concentrations) prevailed, presented a significantly superior incinerability correlation to field tests than any of the other proposed methods of ranking. Those methods included heat of combustion, auto-ignition temperature, theoretical flame-mode kinetics, experimental flame failure modes, ignition delay time, as well as gas-phase thermal stability at high oxygen concentration.

The results of four experimental studies were presented as support to developing/expanding the data base on Principal Organic Hazardous Constituent (POHC) stability and Products of Incomplete Combustion (PIC) formation for pure compounds and mixtures.

Several studies were proposed for further laboratory investigation of the thermal treatment process.

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PIC FORMATION UNDER PYROLYTIC AND STARVED AIR CONDITIONS

INTRODUCTION

The University of Dayton Research Institute (UDRI) has addressed various incineration issues in the first 18 months of the Cooperative Agreement CR-810783-01-0 and has produced upwards of 15 publications/ presentations based on the several projects during that period. However, the projects encompassing "PIC Formation Under Pyrolytic and Starved Air Conditions" is emphasized in the following report.

The ultimate goal of incineration research is to understand the process of incineration to the extent that one can accurately predict incinerator emissions and how changing design and operational parameters affect pollutant emission rates.

Emissions of hazardous organic compounds fall into two general categories, those compounds in the waste feed which are not totally destroyed and those compounds formed from the partial degradation of the waste. Designations for these classes have been borrowed from the regulatory designations of Principal Organic Hazardous Constituents (POHCs) and Products of Incomplete Combustion (PICs). Since regulation of incineration will always require some type of testing or monitoring of the actual incinerator, a desirable product of research would be information that can be used to reduce the testing burden and ensure that the proper emissions and operating parameters are being monitored that will ensure environmentally safe waste disposal. This has been the goal of the research program conducted by UDRI.

The complexity of the incineration process, the differences in incinerator designs, and the difficulties in monitoring changing operating conditions makes the accurate prediction of <u>absolute</u> incineration performance an essentially impossible task. A more reasonable goal is to be able to predict the <u>relative</u> destruction efficiency of POHCs and the relative emission rate of PICs for a given incinerator. This is a goal which is consistent with the goal of reducing the need for incinerator testing, since one could then simply conduct tests focusing on the least "incinerable" POHCs and the PICs of greatest yield as predicted by laboratory testing and research. If these compounds are found to meet regulatory requirements then presumably so would the other POHCs and PICs. Of course, one must have sufficient knowledge of the effect of incineration parameters on POHC and PIC emissions to correctly define the conditions for the labora-

tory and field studies and allow for subsequent changes in these conditions on the incinerator. Laboratory and field testing under "worst" case conditions would appear to be the best means of assuring continuing incinerator compliance. Once initial compliance has been established, a method of monitoring for continuing compliance is also necessary. This defines a second goal of our research program which is to identify appropriate species or operating parameters for continuous compliance monitoring.

DEVELOPMENT OF AN INCINERATION MODEL

The first step in determining which incinerator parameters significantly affect POHC and PIC emission is to develop a simple, qualitative incineration model that can be used to determine major effects.

In determining the destruction efficiency of hazardous organic materials by incineration, chemical reactions occuring in condensed phases may effectively be neglected. This is true due to mass and heat transfer considerations. Thus, we may primarily concern ourselves with gas-phase chemistry although the nature of the passage of material from condensed phase into the gas-phase by physical processes may be important.

Once in the gas phase, there exists more than one mode of destruction of the material and it is necessary to address the factors affecting these destruction modes. Two modes are clearly evident and they may be designated as direct flame and thermal (non-flame) decomposition.

Both flame mode and thermal decomposition studies indicate that any known organic waste can be destroyed in an incinerator to greater than 99.99% destruction efficiency (DE) if it is operating under theoretically optimum conditions (1-3). Thermal decomposition can be expected at less than 1000C in flowing air at a mean residence time of 2.0 seconds. Flame destruction of waste droplets may occur in flames operating in excess of 850C.

Excursions, or fault modes, are probably the controlling phenomena for incineration efficiency. Four parameters (atomization inefficiency, mixing inefficiency, thermal failure, and quenching) have been identified as failure modes in flames (2). Laboratory studies have shown that relatively small excursions from ideality for these parameters can easily drop measured flame destruction efficiencies from greater than 99.99% to 99% or even less than 90% (three orders of magnitude). Non-flame upset parameters can be conveniently classified in terms of distributions of oxygen, residence time, and temperature (1-4).

The key to understanding the significance of upset conditions is that only a very small fraction of the total volume of the waste needs to experience these less than optimum conditions to result in significant deviations from the targeted destruction efficiencies. To illustrate how

laboratory thermal decomposition testing relates to upset modes and can potentially be used to predict observed emissions from full scale facilities, let us examine a specific example.

Previous research has shown that the destruction kinetics of typical hazardous organic compounds can be described satisfactorily using simple pseudo-first order kinetics (1). Although different or more complex models may be used, the actual model used is not important for the scope of this discussion.

We will first examine the case of a simple one-stage combustor where a waste feed mixture is fed directly into a turbulent flame and the hot gases evolving from the flame pass on through a relatively long, high temperature hold-up zone prior to exiting from the system. Representative reaction conditions for the flame can be chosen as an average residence time of 0.1 second and a bulk flame temperature of 1700K. For the post-flame zone, we may choose a mean residence time of 2.0s and a bulk gas-phase temperature of 1100K. Although a range of residence times and temperatures are actually experienced by the individual molecules, the values chosen are typical effective residence times and temperatures.

As mentioned in the previous paragraphs, several destruction failure modes have been identified for the flame. In this model, we will assume that only 1% of the waste feed avoids experiencing the bulk reaction conditions in the flame. This might be caused by a reduced gas-phase residence time from an improperly operating nozzle or from experiencing a reduced temperature as a result of being sealed in particulate matter. A third cause might be reduced time at temperature from quenching by cold gases or poor mixing with oxygen.

This one percent of the waste feed enters the post-flame zone. The overall measured destruction efficiency at the stack is the weighted average of the destruction efficiencies of the flame and post-flame zones. The results of these calculations for hazardous waste of a range of thermal stabilities are shown in Table 1. From examination of the table, it is apparent that each of the compounds is destroyed to essentially the same efficiency in the flame, i.e., greater than 99.99%. In the post-flame region, significant differences in thermal stability are observed.

From examination of the last column of the table, it is apparent that the overall destruction efficiency parallels the destruction efficiency in the post-flame region. The principal value of the overall DE is 99% in all cases, with the variations in DE occurring to the right of the decimal. The destruction achieved in the flame determines the principal value, while the non-flame destruction efficiency determines the approach to four nines.

The overall destruction efficiencies quoted in the table are typical of preliminary results reported for studies on full-scale incinerators. The measured destruction efficiencies for essentially all full-scale systems have exceeded or approached 99.99% for most compounds. Variations have been in the third, second, or in some cases, the first decimal place.

TABLE 1. CALCULATED DESTRUCTION EFFICIENCY FOR REPRESENTATIVE HAZARDOUS ORGANICS

Compound	A (s^{-1})	E_a (kcal/mole)	Calculated Destruction Efficiencies DE (Flame)	DE (Post-Flame)	DE (Overall)
Acetonitrile	4.7×10^{7}	40	99.999+	66.357	99.664
Benzene	2.8×10^{8}	38	99.999+	99.999+	99.999+
Chloroform	2.9×10^{12}	49	99.999+	99.999+	99.999+
Tetrachlorobenzene	1.9×10^{6}	30	99.999+	98.556	99.986
Tetrachloroethylene	2.6×10^{6}	33	99.999+	77.127	99.771
Trichlorobenzene	2.2×10^{8}	38	99.999+	99.968	99.999+

A further observation has been that most incinerators can achieve a DE of 99.99% for essentially all waste feeds when operating optimally. However, optimum operation cannot be attained on a continuous basis. If an incinerator could be sampled on a continuous basis, one would probably find that at least 90% of the hazardous organic emissions occur in the fraction of time when the incinerator experiences an upset. Such upsets could be loss of flame, an overload of waste feed, or a failure of a spray nozzle. It is during these system upsets that a large percentage of the feed material can escape flame mode destruction and the reaction conditions in the post-flame zones can be degraded from their steady-state operating values. Under upset conditions, the difference in waste incinerability may be magnified, the non-flame zone destruction comes to even greater prominence, and the performance of the incinerator fails to achieve four nines for a greater number of components of the waste feed.

Poor mixing of waste and oxygen in the afterburner gives rise to a certain fraction of the waste being subjected only to low oxygen conditions. Numerous laboratory studies have shown that destruction of the feed material is much slower under these conditions and PIC formation is enhanced. We again have the case where although most of the waste experiences oxidizing conditions and is destroyed, the small fraction of the feed experiencing the pyrolytic conditions may be responsible for the emission. The observation in field and laboratory studies that most reaction products are pyrolysis type products (e.g., benzene, toluene, naphthalene) tends to confirm this hypothesis.

Although the conclusion that a subfraction of a fraction of the waste feed is responsible for most hazardous organic emissions may be surprising at first, the same process is generally responsible for emission of most air pollutants. One is not really concerned with the major chemistry, such as in a power plant which forms carbon dioxide and water; but instead the minor reaction pathways which form sulfur dioxide, sulfuric acid, and nitrogen oxides. These pathways are responsible for less than 0.1 to 1% of the stack emissions but are the reactions of interest in pollutant formation.

The applicability of this qualitative model has recently been confirmed by a more complex model of hazardous waste incineration developed by the Energy and Environmental Research Corporation (EERC) [5,6]. This model includes considerations of furnace heat transfer, flow, mixing, injection, tracking, and kinetics. UDRI pseudo-first order thermal decomposition kinetics were used as inputs for the model. Thus far, modeling results for three pilot-scale hazardous waste thermal destruction systems have been reported. These systems are the Controlled Temperature Tower (CTT), the US EPA's Combustion Research Facility's (CRF) rotary kiln system, and the Acurex subscale boiler. The CTT was modeled under several modes of operation and failure modes including standard, cooled, insulated, backheated, fast quench, and various droplet vaporization points. The CRF system was modeled for varying loads, different excess air levels, and kiln or afterburner flameout. The Acurex subscale boiler was modeled for various fuel heating values, heat removal rates, excess air rates, waterwall/nonwaterwall modes, various droplet vaporization points, and temperature profiles.

In each reported case the predicted relative destruction efficiencies correlated almost perfectly with the values for $T_{99.99}(1)$ (temperature for 99.99% destruction at 1.0 sec. residence time) of the test compounds. For the CTT, the agreement was essentially perfect for every case. For the six test compounds modeled for the CRF, only methane exhibited a moderate deviation from the behavior predicted by purely pseudo-first order post-flame kinetics. For the Acurex boiler, of the eight compounds modeled, only acetonitrile showed significant deviation (see Figure 1).

The excellent agreement between the ranking according to $T_{99.99}$ (1) and the EERC model are as predicted by our two-zone incineration model, illustrating the importance of post-flame reaction kinetics. Although quantitative predictions are available from the EERC model, accurate predictions for complex incineration systems will require many years of model development and refinement. However, the significance of post-flame chemistry in controlling relative POHC DEs has been clearly confirmed.

Thus, improvements of model accuracy can best be accomplished by more refined post-flame kinetics. Detailed flame kinetics are of less value since waste compounds subjected to the flame environment will essentially be totally destroyed. Post-flame kinetics can be improved by addressing the effect of varying oxygen levels and waste feed composition for mixtures. Most importantly, the development of data on formation of PICs is essential.

Comparison of UDRI generated laboratory flow reactor (non-flame) data with laboratory flame-mode data, illustrates the similarity in the reaction mechanisms for both zones, i.e., a free-radical degradation mechanism. These results suggest that many PICs can be formed from simple feed mixtures and the POHC DEs and PIC yields may be very dependent upon the waste composition and oxygen level of the reaction atmosphere. A detailed comparison of field and laboratory studies further indicates the importance of PIC emissions in determining incinerator performance and how laboratory data can be used to predict PIC formation.

COMPARISON OF FLAME AND THERMAL DECOMPOSITION RESULTS

With our flow reactor systems at UDRI, we have generated thermal decomposition data on nearly 100 different hazardous organic compounds. The experimental difficulties in generating similar flame data has resulted in a very limited data base for comparison. However, a recently reported study has furnished some data for comparison (7).

Thirteen compounds of interest to hazardous waste incineration were combusted in a laboratory diffusion flame. The relative burning rates of these compounds were determined based on their flame front velocities. A listing of these compounds and their rankings based on non-flame thermal degradation studies is shown in Table 2. For the six compounds for which thermal decomposition data is available, the non-flame rankings are indicated. Furthermore, the flame-mode rankings for the remaining compounds are basically as one would predict for the thermal degradation of untested compounds.

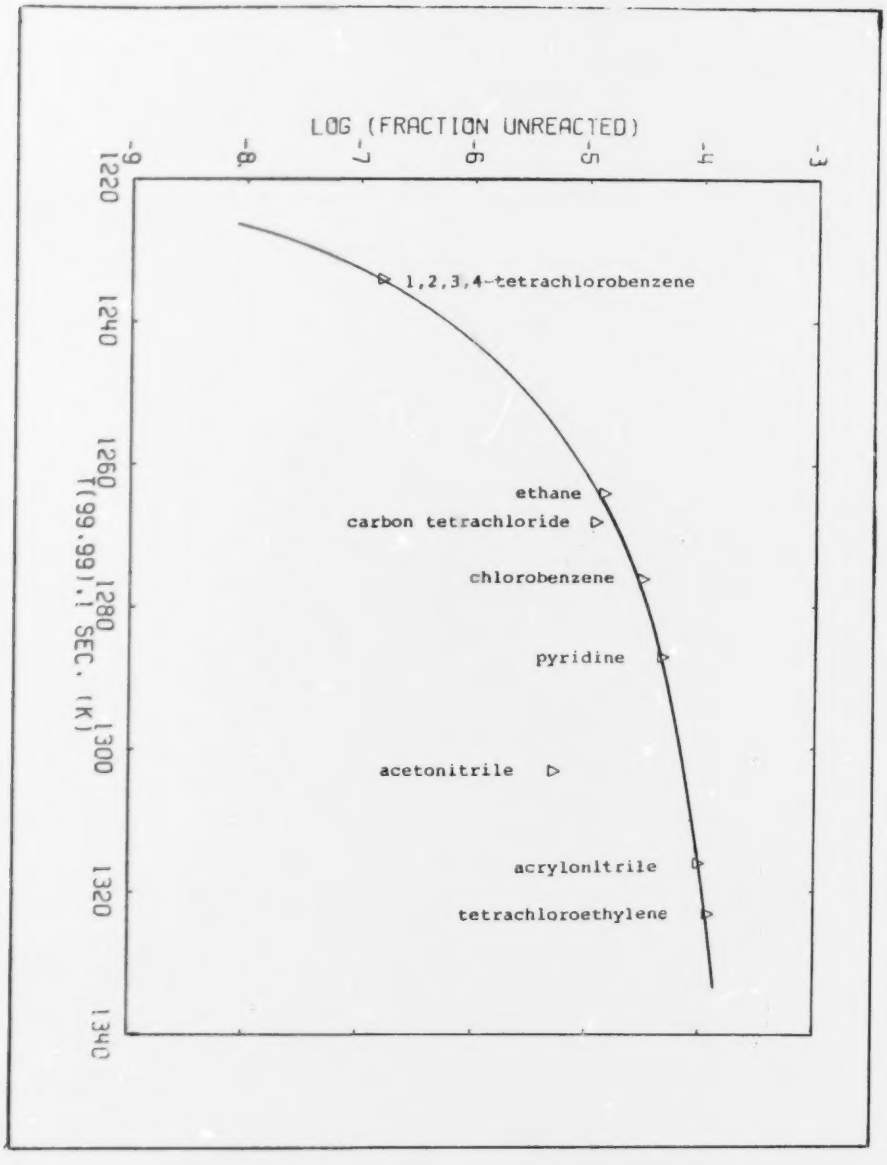

Figure 1. Comparison of EERC model prediction with predictions of UDRI two-zone incineration model for the Acurex Subscale Boiler. The results indicate the control of overall relative destruction efficiencies of test compounds by post-flame chemical kinetics.

TABLE 2. COMPARISON OF FLAME AND NON-FLAME (THERMAL) STABILITY RANKING OF VARIOUS TEST COMPOUNDS

Compound	Relative Burning Rate (Flame)[7]	UDRI Thermal Stability (Non-Flame) Ranking
1,2,4-Trichlorobenzene	10.9	1[1]
m-Dichlorobenzene	13.5	2
o-Dichlorobenzene	12.6	3
1,6-Dichlorohexane	25.6	
Chlorobenzene	28.4	4
1-Chlorohexane	34.7	
Benzene	60.0	5
Dichloroisopropylether	87	
1,2-Dichloropropane	219	
n-Hexane	736	
1,1,1-Trichloroethane	844	6
Epichlorohydrin	1142	
1,2-Dichloroethane	1500	

[1]Ranking of 1 is most stable

In a second flame experiment, various combinations of dichlorobenzene, benzene, and hydrogen chloride (HCl) were combusted at 40% of stoichiometric air. The identity and yield of these products were found to be essentially invariant as long as the ratios of chlorine, hydrogen, carbon, and oxygen were constant. The observed PICs are listed in Table 3.

Recently completed was a study of PIC formation from the thermal decomposition of a mixture of carbon tetrachloride, toluene, chlorobenzene, trichloroethylene, and Freon 113 (4). Those PICs resulting from this mixture that were also found in the flame combustion of chlorobenzene are also noted in Table 3.

The agreements between relative POHC stability and PIC production for flame and non-flame studies is striking, particularly for PIC production. Most of the differences in observed PICs are the lack of higher chlorinated compounds from the thermal degradation studies. This is probably due to the fact that the chlorine content of the thermal degradation mixtures was only 6 mole percent while it was 50 mole percent for the flame study, the latter favoring formation of higher chlorinated species. The only other real discrepancy was the lack of formation of biphenylene and chloroacetylene in the thermal decomposition study, although the presence of chloroacetylene was suspected from Gas Chromatograph (GC) analysis but could not be confirmed by Gas Chromatograph-Mass Spectometer (GC/MS) due to experimental limitations.

The similarity in results obviously suggests that similar reactions are occurring, i.e., a gas-phase free-radical mechanism. It is well documented that hydrocarbon reactions proceed by mechanisms based primarily on attack of molecular species at low temperature (3,8). At temperatures between 250 and 450C, a peroxide-dominated mechanism appears to be active. Above 450C, transition to a free-radical mechanism usually occurs.

The "knee" in the thermal decomposition profiles generated on the TDAS (Thermal Decomposition Analytical System) and TDU-GC (Thermal Decomposition Unit-Gas Chromatograph) denotes the region of transition from a relatively slow to a much faster reaction mechanism, e.g., transition from a peroxide to a free-radical mechanism (see Figure 2 for example). Detailed kinetic calculations for propane indicate a rapid increase in the concentration of the free-radical pool, predominantly OH, O, and H, in the temperature range of the knee (see Figure 2). We have also performed pseudo-equilibrium calculations for other more complex molecules, which also demonstrate a rapid increase in radical concentration in this region. This temperature range of 500C to 700C is also appropriate for unimolecular decomposition reactions to become significant.

Some resarchers have questioned the contributions of surface reactions or "wall effects" on flow reactor studies. We have compared the results of the extended gas-phase kinetic model for propane oxidation with results from the TDU-GC. This kinetic model has previously been compared to results from shock-tube studies and shown to be in excellent agreement (9). As can be seen from the graph in Figure 3, the agreement between this purely gas-phase kinetics model and our flow reactor study is excellent,

TABLE 3. PICs FOUND IN DIFFUSION FLAME COMBUSTION OF CHLOROBENZENE, BENZENE, AND HCl MIXTURE AND THERMAL DECOMPOSITION OF A MIXTURE OF CARBON TETRACHLORIDE, TOLUENE, CHLOROBENZENE, TRICHLOROETHYLENE, AND FREON 113

	PICs From:	
	Flame-Mode Combustion	Thermal Decomposition
	Mixture 1	Mixture 2
Anthracene	x	x
Benzofuran	x	x
Biphenyl	x	x
Biphenylene or Acenaphthalene	x	
Chloroacetylene	x	
Chloroanthracene	x	
Chlorobenzene		x
Chlorobiphenyl	x	
Chlorobiphenylene	x	
Chloronaphthalene	x	x
Chlorophenylacetylene	x	x
Chlorostyrene	x	x
Chlorotoluene	x	x
Dichloroanthracene	x	
Dichlorobenzene		x
Dichlorobiphenyl	x	
Dichloronaphthalene	x	x
Dichloromethylstyrene	x	x
Dichlorostyrene	x	x
Dichloroacetylene	x	x
Dibenzofuran	x	x
Fluoroanthene	x	x
Methylnaphthalene	x	x
Naphthalene (or Azulene)	x	x
Phenylacetylene	x	x
Phenol	x	x
Phenylnaphthalene	x	x
Pyrene	x	x
Styrene	x	x
Tetrachloribiphenyl	x	
Trichlorobiphenyl	x	
Trichlorobenzene	x	
Toluene	x	x

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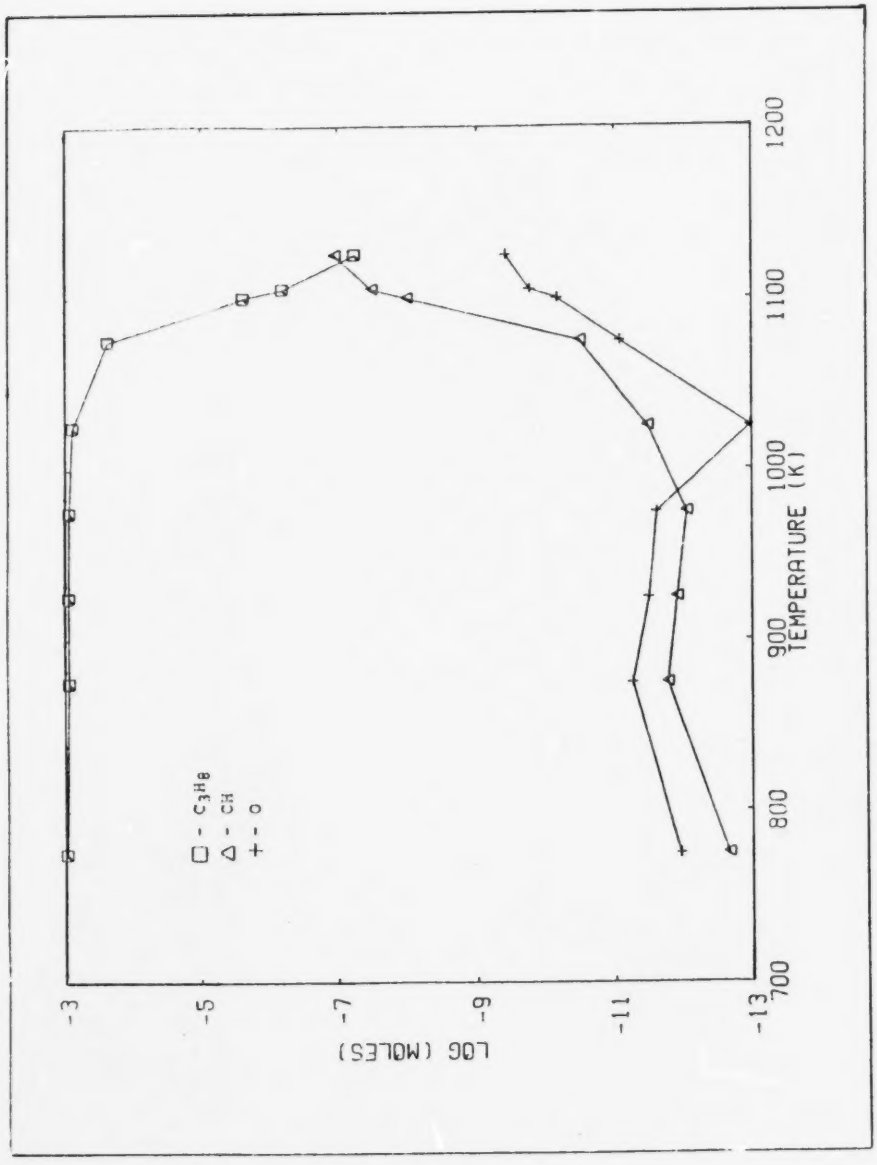


Figure 2. Concentration vs. temperature for propane oxidation in air at a gas-phase residence time of 2.0 seconds.

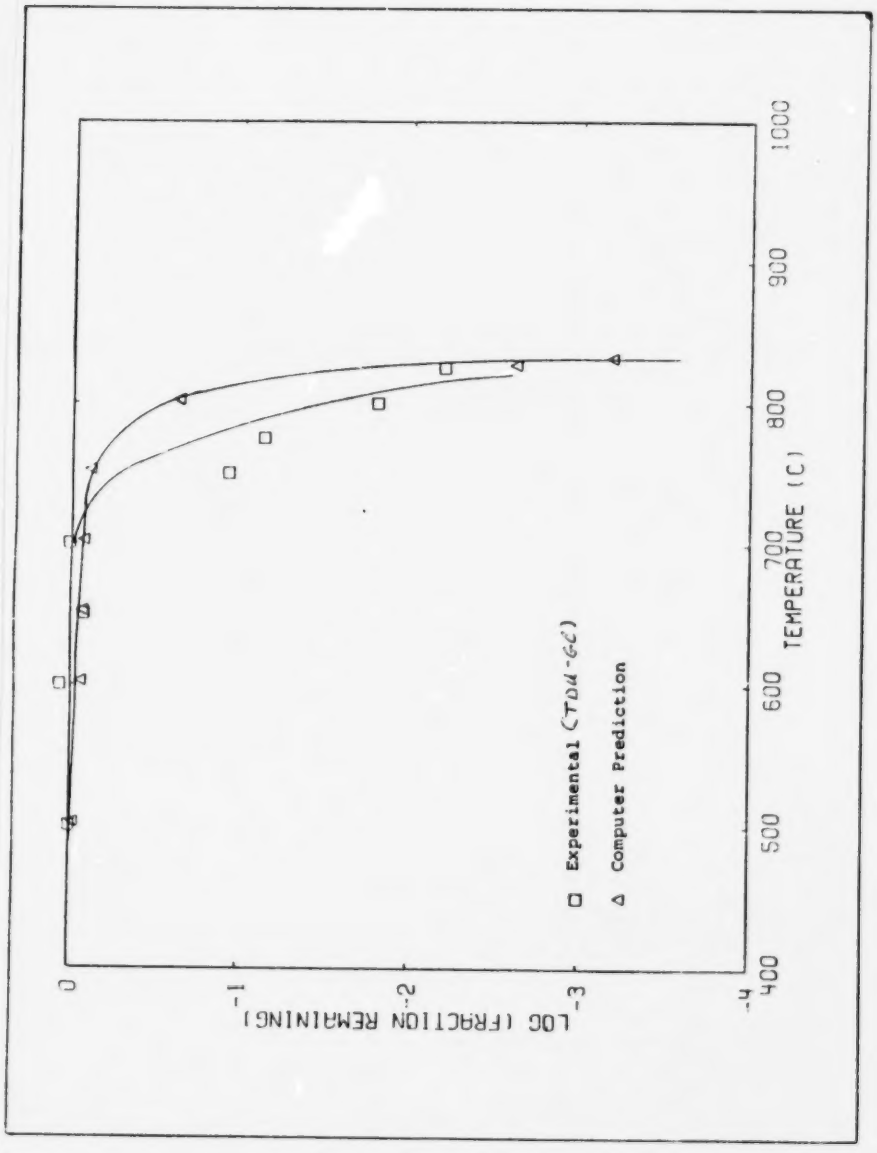


Figure 3. Comparison of flow reactor generated thermal decomposition profile versus predicted results from computer-modeled gas-phase free-radical mechanism for propane oxidation.

especially in predicting the $T_{99.99}(2)$. The slightly faster rate of decomposition predicted by the model in the knee of the curve is likely due to inaccuracies in the model in accounting for reactions involving peroxides. This is not unexpected since the model was developed for a higher temperature region, where free-radical mechanisms dominate. The agreement between the flow reactor study and the gas-phase free-radical kinetic model indicates that the mechanism of propane degradation in the TDU-GC is truly a gas-phase, free-radical pathway at higher temperatures.

There is clearly a demonstrated correlation between flame-mode and non-flame flow reactor POHC and PIC data. This is due to free-radical, decomposition reactions being operational in both instances. The marked agreement in PIC identities, even for dissimilar feed mixtures, further illustrates the importance of the free-radical mechanism. The majority of the products are due to recombination of free-radical fragments or radical addition to aromatic substrates. The lack of oxygen-containing products even under oxidative conditions suggests that abstraction of H by OH and O dominate over addition reactions. Alternately, addition products such as phenols may be very reactive and rapidly undergo further degradation.

The main experimental difference in the flow reactor and flame studies is the higher temperature in the flame which accelerates the overall reaction rate, but apparently does not result in a change of mechanism. Thus, relative POHC DEs and PIC identities are very similar for both cases.

CORRELATION OF LABORATORY PREDICTIONS AND FIELD RESULTS

Of course the ultimate test of the study of the utility of laboratory research is the degree of agreement between experimental or theoretical predictions and actual field results.

It was felt that a comparison of various proposed scales of incinerability with recently available field test results would be useful. If areas of agreement or disagreement could be identified, then considerable guidance could be gained for the direction of future research. This study, which required considerable time and effort, was quite successful. A summary of the results are reported in the following paragraphs.

Six methods of ranking the relative incinerability of hazardous organic compounds have been previously proposed (1,2,4,7,10-14).

- Heat of Combustion ($\Delta H_c/g$)
- Auto-Ignition Temperature (AIT)
- Theoretical Flame-Mode Kinetics (TFMK)
- Experimental Flame Failure Modes (EFFM)
- Ignition Delay Time (IDT)
- Gas-Phase Thermal Stability [$T_{99}(2)$ (99% destruction at 2 seconds residence time), $TSHiO_2$ (High oxygen concentration), $TSLoO_2$ (Low oxygen concentration)]

The gas-phase thermal stability method has been proposed based on the results of flow reactor studies. One method of ranking that has been previously proposed is based on laboratory-determined thermal stability specified by the temperature required for 99% or 99.99% destruction at 2.0 seconds reactor residence time in an atmosphere of flowing air [T_{99} (2)] (1,14). This scale was originally developed for pure compounds in flowing air. However, recently generated data have shown that relative stability varies as a function of the composition of the waste feed and oxygen concentration [4]. This has led to modification of the rankings to account for the thermal stability of individual POHCs fed as a mixture in both an oxygen-rich ($TSHiO_2$) and an oxygen deficient ($TSLoO_2$) environment. These three hierarchies along with the predictions of the other five, have been applied to predicting results of studies described in the following paragraphs.

Intercomparison of field and laboratory data should be conducted with extreme caution. While laboratory studies are usually conducted under precisely controlled well-defined conditions, field studies generally are not (2,4, 14,15). Upon examination of field study reports, it is obvious that the quantitative intercomparison of the performance of the facilities with respect to operational parameters is not viable. However, relative DRE data for POHCs within a waste feed at a given facility can be analyzed with proper data validation guidelines. To ensure a valid comparison of predicted and observed results, the following data validation and reduction criteria were used:

- only compare POHC DREs (Destruction and Removal Efficiencies) for a given incinerator
- only compare POHC DREs when they are fed to the system at a common point
- use averages of DREs when no significant run-to-run variation in relative POHC DRE is observed
- only use data where the majority of the POHC DREs are less than 99.995%
- include data from non-concurrently fed POHCs if other key parameters are held constant
- conduct the correlation of observed field vs. predicted results on a rank/order basis with a minimum of four data points.

The observed incinerability rankings of the test compounds at each source were compared with the prediction of each proposed hierarchy using a rank/order correlation approach (16). This method was judged to be superior to a linear regression analysis since the latter judges the agreement of the data with a best-fit straight line while the former simply determines if a statistically significant relationship exists between the observed and predicted rankings. The rank-correlation coefficient, r_s, was used to judge if a correlation existed at the 90% confidence level for a number of test compounds, N.

TABLE 4. RESULTS OF STATISTICAL ANALYSES OF OBSERVED VERSUS PREDICTED THERMAL STABILITY RANKINGS

Study	Heirarchy							
	H_c/g	AIT	TFMK	EFFM	IDT	$T_{99}(2)$	$TSHIO_2$	$TSLoO_2$
A	-0.300/5[1]	-0.200/4	--	--	--	--	0.000/5	0.900/5*
B	-0.190/8	0.200/4	--	--	--	-0.057/6	0.533/10*	0.529/10*
C	-0.500/5	--	--	--	--	0.500/5	0.400/5	0.600/5
D	-0.100/9	-0.060/	--	--	--	-0.800/4	0.386/9	0.493/9*
E	0.589/7*	0.428/6	--	--	--	-0.300/5	0.425/8	0.429/8
F	0.343/15	0.571/7*	-0.100/5	--	--	-0.425/9	0.041/15	0.073/15
G	0.400/4	--	--	--	--	0.800/4*	0.800/4*	0.900/4*
H	-0.333/7	0.457/6	--	--	-0.300/4	-0.161/7	-0.036	0.655/8*
I	-0.077/10	-0.262/8	0.600/4	0.600/4	-0.100/5	-0.217/9	-0.318/11	0.536/11*
J	-0.291/10	0.147/8	0.800/4*	0.600/4	-0.100/5	-0.202/9	-0.114/11	0.523/11*
# Of Successes	1	1	1	0	0	1	2	7
# Of Failures	9	8	2	2	3	8	8	3
% Success*	10	11	33	0	0	11	20	70

[1] r_s/N

*Correlation was statistically significant at the 90% confidence level

Results of this analysis are summarized in Table 4 for ten studies judged to meet the data validation criteria (15,17-22). Of the eight proposed ranking methods, only $\Delta H_c/g$, AIT, T_{99} (2), $TSHiO_2$, and $TSLoO_2$ had a sufficient data base to make predictions for a significant number of sources. Of these, only the experimentally predicted order under low oxygen conditions, $TSLoO_2$ met with a reasonable success, i.e., 70%. The other four methods only correlated with field observations 10-20% of the time. More importantly, it was apparent after detailed examination of the individual data plots that certain trends were occuring that could not be explained by simple application of the ranking methods. In particular, the compounds that deviated in stability from predictions of the $TSLoO_2$ hierarchy were often the same for the various studies. In many cases, this deviation could be explained using other available information.

The paragraphs that follow discuss the data from the specific sources in a manner that demonstrates how the field-scale observations can be reliably predicted with modifications to the $TSLoO_2$ hierarchy.

Study A. The test compounds followed the order of stability: toluene > methyl ethyl ketone > 1,1,1-trichloroethane > Freon 113. The observed order was the same as predicted by $TSLoO_2$ except for reversal of 1,1,1-trichloroethane and Freon 113. In actuality, both of these compounds are predicted to be relatively very fragile under low O_2 conditions, and the predicted rankings could have been easily reversed. The predicted rankings as pure compounds in flowing air or in a mixture of high O_2 were quite different and did not correlate with the observations. This is consistent with the low O_2 levels noted in the field study reports.

Study B. The predictions of the $TSLoO_2$ method and the observed stabilities agreed quite well with only a few exceptions. Chlorobenzene and dichlorobenzene were observed to be reversed from the predicted order. This is readily explained by the observation that significant levels of chlorobenzene were detected in the scrubber make-up waste and could be stripped out and into the stack gases. This would result in an apparent chlorobenzene DRE lower than actually achieved by thermal destruction and account for the disparity with the $TSLoO_2$. A major deviation was observed for bis-2-ethyl-hexyl phthalate, which appeared more stable than predicted. Although the predicted stability of phthalate is questionable due to lack of laboratory data, phthalates are ubiquitous and detected levels may be due to out-gassing of plastics in the system and not from undecomposed feed. High levels of phthalates are commonly found in ambient environments and for this reason should probably be excluded from all data sets (23). Bis-2-ethyl-hexyl phthalate was found at high levels in the scrubber water. Stripping from the water by the effluent gas could account for its observed emissions.

Two other major outliers were aniline and trichloroethylene. These compounds were significantly more fragile than predicted. Neither aniline nor trichloroethylene would be expected to be a major thermal reaction product from this test sample. This is in contrast to chloroform, carbon tetrachloride, and phosgene, which unexpectedly surpassed aniline and trichloroethylene in apparent stability. The apparent thermal stabilities of

carbon tetrachloride, chloroform, and phosgene may be due to their formation as products from other components of the waste as opposed to their stability as POHCs. Furthermore, these compounds are quite volatile and could be present in the ambient air as fugitive emissions. Either formation as a product or as an ambient air contaminant could explain the unexpected reversal in thermal stability.

Study C. The waste was spiked with theroretically stable POHCs which had an observed order of stability: acetonitrile > benzene > trichloroethylene > chlorobenzene > carbon tetrachloride. This was as expected except for benzene which was considerably more stable than predicted based purely on thermal stability. It is possible that benzene was formed as a product from chlorobenzene (or the auxiliary fuel). This hypothesis is supported by two independent observations. First, a simulated waste stream very close in composition to the actual waste was subjected to thermal decomposition in the laboratory. Under low O_2 conditions, benzene would actually have been predicted as a reaction product resulting in a low apparent DRE for benzene as a POHC. Secondly, the waste stream was also fed to the full-scale incinerator without benzene in the feed. Roughly equivalent levels of benzene were found in the stack effluent, thus confirming the hypothesis that its emission was due to sources other than residual POHC from the waste feed.

Study D. Field test results were in basic agreement with prediction for low oxygen conditions. The exceptions were phthalates, which were discussed previously, and tetrachloroethylene, which was predicted to be the most stable component but was observed to be less stable than benzene, toluene, naphthalene, carbon tetrachloride, and methyl ethyl ketone. Laboratory studies have demonstrated or strongly suggested that each of these compounds can be a significant reaction product from various precursors (4,17,24). Dichloromethane and chloroform were also found in the source emissions, suggesting the formation of chlorinated methanes as thermal reaction products. Thus, the apparently greater stability of these compounds than tetrachloroethylene may be due to their formation as products in the incineration process.

Study E. A correlation was observed between predicted and observed rankings but there was significant scatter. The fragile nature of 1,1,2-trichloroethane, 1,1,1-trichloroethane, and methyl ethyl ketone were correctly predicted (DREs all at 99.999% or greater). The observed stability of these three compounds were permuted from their predicted value contributing to the poor correlation coefficient.

Methylene chloride, and to some extent, carbon tetrachloride appeared more stable than predicted. It should be noted that high levels of other halogenated methanes were found in the stack effluent indicating a source of carbon tetrachloride and methylene chloride emissions other than residual POHC (i.e., either incomplete combustion products or a result of stripping of these volatiles from the scrubber water). The most unexpected behavior was exhibited by tetrachloroethylene, which was predicted to be the most stable POHC but was observed to be very fragile.

Study F. Although this facility exhibited the lowest correlation of predicted and observed emissions, the results are extremely informative. Two distinct groups were evident, one consisting of primarily chlorinated aromatics and olefins, and a second consisting of primarily halogenated aliphatics along with bis-2-ethyl-hexyl phthalate and hexachlorocyclobutadiene.

Methylene chloride and chloroform were found in the scrubber make-up water which could readily account for their observed emission levels. The other halogenated compounds (in the second group) are also very volatile and have been found in the ambient air surrounding such facilities (presumably due to fugitive emissions) (15). As previously discussed, phthalate emissions are consistently high at most sources. Finally, there is some question concerning the accuracy of the predicted ranking for hexachlorocyclopentadiene due to lack of laboratory data. Its low stability prediction was based on possible strain of the five numbered ring structure, but could well be in error. If the six compounds in question are eliminated from the data set and a correlation is performed with the remaining nine compounds, a statistically significant rank correlation coefficient of 0.89 is obtained.

Study G. The observed stability is as predicted under low O_2 conditions except for carbon tetrachloride which appeared more stable than chlorobenzene. This is not surprising since chloroform, which was also present in the mixture of carbon tetrachloride, has been established as a thermal reaction product of chloroform by laboratory studies.

Study H. The POHCs in this test essentially followed the predicted order except for tetrachloroethylene and trichloroethylene, which appeared less stable than benzene and toluene, contrary to predictions. This type of result has been observed in other studies and is ascribed to the propensity for formation of toluene and benzene as reaction products. It is also interesting to note that carbon tetrachloride emissions were also quite high (average of 173 g/s) which tends to confirm its prevalence as a reaction product from incineration of chlorinated wastes.

Study I. The observed POHC stabilities followed predicted trends except for benzene, carbon tetrachloride, and 1,2-dichloroethane. Benzene and carbon tetrachloride are again expected to be products of thermal degradation (primarily from chlorobenzene/toluene and methylene chloride respectively). The 1,2-dichloroethane is a volatile compound that is commonly found in scrubber water or in the ambient air as a fugitive emission, factors which could account for its elevated emission level (15). The emission level of 1,1,1-trichloroethane, also sometimes found as a fugitive emission or in scrubber makeup water, was also slightly elevated.

Study J. The observed deviations from the predicted rankings were similar to those observed for the previous nine cases. Benzene, toluene, and carbon tetrachloride emissions were higher than expected, an observation which is attributed primarily to product formation.

Discussion of Laboratory/Field Comparisons

The degree of success, as indicated by the results reported in Table 4 and the subsequent discussions of predicting the relative thermal stabilities of hazardous organics through laboratory flow reactor studies may appear somewhat surprising considering the complexity of the incineration process. However, the development of the two-zone incineration model, which was discussed earlier illustrates how post-flame chemistry controls incinerator emissions and is sufficient to explain general agreement between laboratory-based predictions and field results. However, none of the previously presented incinerability hierarchies directly address the issue of PIC emissions as they are only concerned with thermal stability of the POHCs in the feed material.

PICs resulting from the incineration of hazardous waste are not currently regulated by the USEPA. However, the previously discussed field data and results of other laboratory, pilot, and full-scale testing programs have shown that toxic products can be formed and are emitted from incinerators (3,4,17-24). Many observed PICs are also potential POHCs, consequently, it is entirely possible that a PIC may also be a POHC in the original mixture. Three documented examples are: the formation of carbon tetrachloride from chloroform, and from hexachlorobenzene from hexachlorocyclopentadiene, and benzene from chlorobenzene or toluene (4,17,24).

In the previous discussion of field results many such cases were identified. This gave rise to low apparent DRE for the POHC. Since this effect would be more important when the input concentration of the POHC is low, the result would be an apparent dependence of DRE on input POHC concentration (i.e., the higher the input concentration, the greater the apparent DRE). The true effect, however, is that the emission concentration is constant, since the emissions are probably due to product formation from other waste components.

The observation of an apparent DRE dependence on concentration has been made for hazardous waste incinerators and attributed to greater than first order kinetics for indivudal POHCs (15). While such an effect could be possible for combustion of a pure compound, it is highly improbable when the POHC is only a small portion of a complex waste. The reaction chemistry is determined by the overall waste and fuel composition as opposed to pure compound kinetics. Volatile POHCs in the ambient air as a result of fugitive emissions, volatile POHCs stripped from scrubber waters, and out-gasing of phthalate-containing materials would also give rise to apparent concentration dependencies since their emission levels would be constant while the POHC input rate varies. Specifically, it has been shown earlier that most of the observed deviations from laboratory predicted rankings of incinerability may be attributed to product formation or "contamination" of the stack effluent by volatile POHCs that did not pass through the destruction zones of the incinerator.

As if predicting POHC stability were not difficult enough, we must now predict product formation. This can be accomplished perhaps by laboratory thermal decomposition testing of the actual waste stream to be incinerated,

or a very close simulation. As indicated by the agreement of laboratory predictions based on low O_2 conditions, these studies should be conducted under pyrolytic conditions.

An excellent example of this approach is Study C. The incinerability ranking based purely on POHC DRE was successful for four out of the five constituents of the waste, only benzene being apparently more stable than the other components. However, laboratory testing was performed on a very similar waste stream and under pyrolytic conditions; significant levels of benzene were were observed. Thus, when product formation is included, laboratory testing of a simulated waste stream could correctly predict the observed field results.

Summary And Conclusions Regarding Laboratory/Field Comparisons

The results of comparison of ten field studies with thermal stability predictions indicates that no ranking based on pure compound properties can provide an appropriate scale of incinerability. However, a ranking based on predicted POHC stability in complex mixtures under low oxygen conditions gave a statistically significant correlation with field results in seven of ten cases. More importantly, analysis of results gives strong reason to believe that formation of "POHCs" in the incineration process as PICs may be responsible for their observed DREs.

Pending further confirmatory comparisons with field results, the following conclusions are proposed.

- Measured POHC DREs and relative stabilities of all but the most stable compounds are due to formation as products from other components of the waste fuel or feed.
- Only DREs for very stable POHCs, or POHCs difficult to form as reaction products (e.g., acetonitrile), are expected to be unaffected by PIC formation and these stabilities are predictable from pure compound thermal decomposition kinetics.
- The stack emissions and observed DREs of the very volatile compounds (e.g., methylene chloride, chloroform, di- and trichloroethanes) may be dominated by fugitive emissions in the ambient air or stripping of these compounds from contaminated scrubber water.
- Thermal decomposition, not in-flame destruction determines relative POHC DREs and the identity and yield of products of incomplete combustion.
- Pyrolytic conditions in the incinerator are responsible for most emissions and control the relative DREs of POHCs and the formation of products.
- Predictions from laboratory thermal decomposition testing of pure compounds and mixtures can be effectively used to predict relative POHC DREs.

- Laboratory testing under pyrolytic conditions on actual waste streams or closely simulated waste streams is an effective and reliable method for predicting relative POHC stabilities and PIC emissions.

EXPANSION OF DATA BASE ON POHC STABILITY AND PIC FORMATION FOR PURE COMPOUNDS AND MIXTURES

The success in predicting the results of field studies from laboratory experimentation shows the utility of the laboratory approach but also points out the need for a larger data base from which to predict the effect of changing reaction atmosphere and waste composition.

The results of four early experimental studies are detailed in the following paragraphs.

Thermal Decomposition of "CRF Soup - 1"*

In our most ambitious laboratory study to date, the thermal degradation of a mixture of five hazardous organic compounds under a variety of conditions was investigated. The mixture was studied in three reaction atmospheres: oxygen-starved, stoichiometric oxygen, and oxygen-rich. The behavior of the components in the mixture was compared to their behavior when tested as pure compounds and the thermal reaction products were identified. Thermal decomposition behavior was analyzed and related to elementary chemical reaction kinetics.

The observed thermal stabilities for the test compounds for each experimental condition are summarized in Table 5. As can be seen from these results, considerable differences in absolute and relative thermal stabilities were observed as a function of both oxygen content (specified as the equivalence ratio, ϕ) and composition of the waste (pure compounds vs. mixture). Furthermore, over 150 thermal reaction products were observed on the TDU-GC. Chlorobenzene was the most stable POHC under pyrolytic conditions while the major reaction product was benzene (although many others had significant yields).

The thermal behavior of these compounds may be explained by examination of possible elementary reaction pathways. The carbon-chlorine bound energy in carbon tetrachloride is 70 kcal/mole and is expected to be less than 78 kcal/mole for Freon 113. Thus, these molecules might be expected to undergo unimolecular decomposition by simple bond rupture and therefore their thermal stability be independent of reaction atmosphere.

In contrast, the degradation of trichloroethylene, toluene, and chlorobenzene is expected to be due to attack of free radicals such as OH, O and H. Since the absolute and relative concentrations of these species will vary depending on the equivalence ratio and waste composition, the

*Simulated Hazardous Waste Mixture #1 tested recently at EPA's Combustion Research Facility in Pine Bluff, Arkansas (CRF)

TABLE 5. SUMMARY OF THERMAL DECOMPOSITION TESTING FOR COMPONENTS OF HAZARDOUS WASTE MIXTURE #1

POHC	ΔH_c/g	T_{99} (2) (°C) for HWM-1 ϕ=0.06	ϕ=1.0	Pyrolysis	T_{99} (2) (°C) Pure Compounds ϕ=1.0	ϕ<<1.0
Freon	0.11	770	780	780	780	780
Carbon tetrachloride	0.24	670	680	680	750	750
Trichloroethylene	1.74	730	780	920	800	780
Chlorobenzene	6.60	730	800	>1000	900	700
Toluene	10.14	670	750	820	820	680

measured thermal stabilities will also vary with changing reaction atmosphere. The lower concentration of H atoms (and somewhat lower reactivity versus OH and O) results in slower destruction rates for the three aromatic compounds at reduced oxygen levels, while Freon 113 and carbon tetrachloride are relatively unaffected. For these reasons, relative POHC thermal stabilities are observed to change as a function of ϕ.

Benzaldehydes, phenols, and benzofurans were the only observed oxidation products under oxidative or pyrolytic conditions while numerous complex pyrolysis type products were observed (see Table 6). This indicates that most products result from recombination of radical fragments and OH and O addition products are not significant. The lack of addition products suggests that OH and O may be more likely to participate in abstraction reactions at high temperatures or that the intermediate addition products are not very stable. This is clearly an area for further research.

In that same study, the thermal degradation of carbon tetrachloride and Freon 113 were observed to be independent of the oxygen content of the reaction atmosphere, while trichloroethylene, monochlorobenzene, and toluene decomposed more readily as the oxygen concentration was increased (see Figure 4 for example). This behavior is predictable based on chemical kinetic considerations as previously discussed. It is also interesting to note that Freon 113 (a previously proposed tracer) was not observed to be very stable. The relatively fragile nature of Freon 113 has recently been confirmed by pilot and field studies [30,31].

Formation of PCDFs and other PICs from PCBs

The thermal degradation of a single PCB isomer was conducted under four reaction atmospheres at a constant gas-phase residence time of 2.0 seconds. The isomer selected for study was 2,3',4,4',5-pentachlorobiphenyl (2,3',4,4',5-PCB). The oxygen availability in the reaction atmosphere was again described using the equivalence ratio ϕ. The values of ϕ used in this study were 3.0, 1.0, 0.2, and 0.05 which range from oxygen starved to very oxygen rich conditions as the values of ϕ become progressively smaller. Thermal degradation experiments were conducted at various temperatures ranging from 500-1000C.

Table 7 lists the major thermal reaction products tentatively identified for the thermal degradation of 2,3',4,4',5-PCB. A variety of pyrolysis and partial oxidation products were formed, with polychlorinated dibenzofurans (PCDF) congeners representing the majority of the oxidative products. Significant quantities of partially dechlorinated biphenyl congeners were formed along with dichlorobenzenes and trichlorobenzenes. Tetrachlorobiphenylene isomers were also observed. These are of particular interest due to their suspected toxicity. The formation of trichloronaphthalene is important because of its apparent thermal stability. At 1000C for ϕ = 1.0, the reaction product tentatively identified as tetrachloronaphthalene exceeded the concentration of the remaining parent PCB. As one might expect, the yield of pyrolysis products decreased with increasing oxygen levels. However, the increase in PCDF concentration with increase in oxygen concentration was far more striking.

TABLE 6. REACTION PRODUCTS OBSERVED FROM THE THERMAL DECOMPOSITION OF CRF SOUP-1

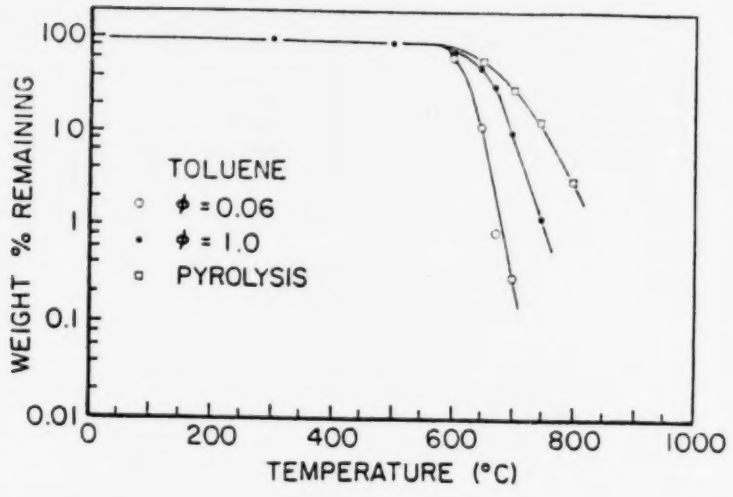
Formula	Identification	ϕ=0.06	ϕ=1.0	Pyrolysis
$CHCl_3$	Trichloromethane	x		
$C_2H_3ClF_2$	Chlorodifluoroethane		x	
$C_2H_2Cl_2$	1,1-Dichloroethene	x	x	x
C_2Cl_3F	Trichlorofluoroethene		x	x
C_2Cl_4	Tetrachloroethene		x	
$C_4H_4Cl_2$	Dichlorobutadiene		x	
C_6H_6	Benzene	x	x	x
C_6H_6	1,5-Hexadiyne 1,5-Hexadien-3-yne	x	x	x
C_6H_6O	Phenol	x	x	x
C_6H_5F	Fluorobenzene		x	x
$C_6H_5C_{10}$	Chlorophenol	x	x	
$C_6H_4Cl_2$	Dichlorohexadiyne Dichlorohexadiene-yne		x	
$C_6H_4Cl_2$	Dichlorobenzene	x	x	
C_7H_8O	Methylphenol	x	x	
C_7H_7Cl	Chloromethylbenzene	x	x	x
$C_7H_6O_2$	Hydroxy-benzaldehyde Benzodioxol	x		
C_7H_6O	Benzaldehyde	x	x	
C_8H_{10}	Ethylbenzene	x	x	x
C_8H_8	Ethenylbenzene (Styrene)	x	x	x
C_8H_7Cl	Chloroethenylbenzene	x	x	x
C_8H_6	Ethynylbenzene	x	x	x
$C_8H_6Cl_2$	Dichloro-ethenylbenzene Chloroethenyl-chlorobenzene Dichloroethenylbenzene	x	x	x
C_8H_6ClF	Chloro-fluoroethenyl-benzene		x	x
$C_8H_6F_2$	Difluoro-ethenylbenzene		x	x
C_8H_6O	Benzofuran	x	x	
C_8H_5Cl	Chloro-ethenylbenzene			x
$C_8H_5Cl_3$	Trichloroethenylbenzene	x		
C_8H_5ClO	Chlorobenzofuran	x	x	x
$C_8H_5F_3$	?			x
C_9H_8	1H-indene		x	x
$C_9H_8Cl_2$	Dichloro-propenylbenzene Dichloropropylbenzene Chloropropenylchlorobenzene	x		x
C_9H_8O	Phenyl-propenal	x		
$C_9H_7Cl_3$	?		x	x
C_9H_7ClO	Chloromethylbenzofuran		x	
C_9H_6O	Phenylpropynone	x		
$C_{10}H_8$	Azulene Naphthalene Methylene-1H-indene		x	x

TABLE 6. - Continued

Formula	Identification	ϕ=0.06	ϕ=1.0	Pyrolysis
$C_{10}H_8ClF$	?			x
$C_{10}H_7Cl$	Chloronaphthalene			x
$C_{10}H_6Cl_2$	Dichloronaphthalene	x	x	x
$C_{10}H_5Cl_3$	Trichloronaphthalene	x		
$C_{11}H_{10}$	1-Methyl-naphthalene		x	
$C_{11}H_{10}$	2-Methyl-naphthalene		x	
$C_{11}H_{10}$	Methyl-naphthalene			x
$C_{12}H_{10}$	Biphenyl		x	x
$C_{12}H_8O$	Dibenzofuran	x	x	
$C_{13}H_{12}$	1,1-Methylene(bis)-benzene			x
$C_{13}H_{10}$	9H-Fluorene		x	x
$C_{13}H_{10}O$	Diphenylmethanone	x		
$C_{13}H_8O_2$	9H-Xanthen-9-one	x	x	
$C_{14}H_{14}$	1,1'-(1,2-ethanediyl)(bis)-benzene	x	x	x
$C_{14}H_{12}$	Methylfluoroene			x
$C_{14}H_{12}$	1,1'-(1,2-ethenediyl)(bis)-(E)-benzene		x	
$C_{14}H_{12}$	Dihydrophenanthrene	x		x
	1,1'-(1,2-ethynediyl)(bis)-(z)-benzene			
$C_{14}H_{10}$	1,1'-(1,2-ethynediyl)(bis)-benzene	x	x	x
	Phenanthrene			
	9-Methylene-9H-fluoroene			
$C_{14}H_{10}O$	Anthracenone	x	x	
	Penanthrenol			
$C_{14}H_9F$	Fluoro-1,1'-(12,-ethyne-diyl)(bis)-benzene			x
	Fluorophenanthrene			
	Fluoromethylene-9H-fluoroene			
$C_{15}H_{12}$	?		x	
$C_{15}H_2$	Methyl-anthracene			x
	Methyl-phenanthrene			
	2-Phenyl-1H-indene			
	9-Ethylidene-9H-fluoroene			
$C_{16}H_{12}$	1,4-Dihydro-1,4-ethenoanthracene		x	x
	1-Phenyl-naphthalene			
	5-Methylene-5H-dibenzo[a,d] cyclo-heptene			
$C_{16}H_{12}$	2-Phenyl-naphthalene		x	x
$C_{16}H_{11}F$	Fluorophenylnaphthalene			x
	Fluoro-5-methylene-5H-dibenzo[a,d]-cycloheptene			
	Fluoro-1,4-dihydro-1,4-etheno-anthracene			

TABLE 6. - Continued

Formula	Identification	ϕ=0.06	ϕ=1.0	Pyrolysis
$C_{16}H_{11}F$	Fluorophenylnaphthalene			
$C_{16}H_{10}$	Pyrene			x
	Fluoroanthene			
$C_{16}H_{10}ClF$	?			x
$C_{16}H_9F$	Fluoropyrene			x
	Fluorofluoroanthene			
$C_{17}H_{12}$	11H-Benzo[a]fluorene			x
	11H-Benzo[b]fluorene			



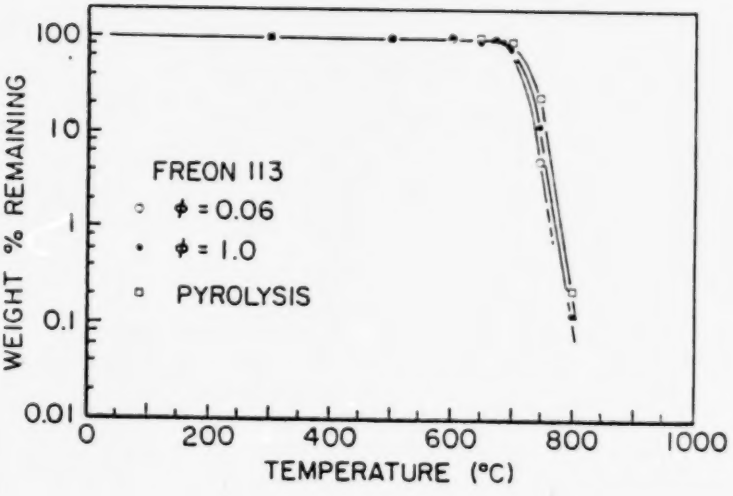


Figure 4. Thermal decomposition behavior of toluene and Freon-113 under fuel lean (ϕ = 0.66) and stoichiometric air (ϕ = 1.0), and absolute pyrolytic conditions for gas-phase residence times ($\bar{t}_r$) of 2.0 seconds.

TABLE 7. MAJOR REACTION PRODUCTS TENTATIVELY IDENTIFIED FROM THE THERMAL DEGRADATION OF 2,3',4,4',5-PENTACHLOROBIPHENYL

Product Class	Number of Major Peaks
Tetrachlorodibenzofurans	2
Trichlorodibenzofurans	2
Pentachlorodibenzofurans	1
Tetrachlorobiphenyls	5
Trichlorobiphenyl	1
Trichlorobenzene	1
Dichlorobenzene	1
Trichloronaphthalene	1
Tetrachloronaphthalene	1
Trichlorophenylethyne	2
Dichlorophenylethyne	1
Tetrachlorobiphenylenes	2
C_9H_8OCl	1
$C_{10}H_3Cl_3$	1

Table 8 presents the yields of observed PCDFs at various equivalence ratios. As the oxygen concentration increased by a factor of 60, the yield of total PCDFs increased by a factor of 7. The percentage of total PCDFs identified as tetra isomers ranged from 62-72%. Thermal formation/destruction profiles for observed PCDFs for ϕ = 1.0 are depicted in Figure 5.

As can be seen from the data in Figure 5 the degradation rate of 2,3',4,4',5-PCB rapidly increases above approximately 750C. This is in the region where one would expect a transition from a peroxide-dominated reaction mechanism to a free-radical mechanism. Pseudo-equilibrium calculations of the concentration of small reactive species indicate that the concentration of reactive radicals increases rapidly between 700C and 900C. Since incorporation of oxygen is necessary for the formation of PCDFs from PCBs, OH and O are implicated as the predominant reactive species responsible for PCDF formation.

For all but the most fuel-rich systems and temperatures between 700C and 1000C, the OH concentration is calculated to be roughly a factor of 10 greater than the O concentration, which is in turn a factor of 1000 to 10,000 greater than the H concentration. Thus, OH would appear to be the major reactive radical under either stoichiometric or oxygen-rich conditions. When the equivalence ratio increases, the OH and O concentrations decrease as the H atom concentration increases. This shift in equilibrium to non-oxygen containing radicals results in a decreased yield of oxygenated products such as PCDF. Thus, for large equivalence ratios, larger yields of pyrolysis products (e.g., polychlorinated benzenes, PCB congeners, chlorinated naphthalenes, chlorinated biphenylenes, etc.) are observed. Although H atoms are usually considered to be the dominant reactive radical in hydrocarbon systems under pyrolytic conditions, the large concentration of Cl atoms in PCB systems may result in Cl being the dominant reactive species. Additional research on the role of Cl atoms is strongly suggested.

For the range of oxygen levels studied, the PCDF yield decreased with equivalence ratio. Although not addressed directly in this study, one might expect the yields of PCDFs to start to eventually decrease with increasing oxygen concentration due to enhanced destruction of the PCDF product as it is oxidized to simpler products including carbon monoxide and carbon dioxide. The shift in the temperature for maximum yield of PCDFs as a function of equivalence ratio is a reflection of the competition between oxidation of PCB to form PCDF and oxidation of the PCDF itself. The observation that the highest temperature of maximum PCDF yield is for ϕ = 1.0 and decreases for ϕ = 3.0 or ϕ = 2.0, may well be due to the shifting concentrations of the species responsible for PCDF formation and destruction.

Potentially important elementary reactions for PCDF formation by OH attack are shown in reactions 1 through 3.

TABLE 8. MAXIMUM WEIGHT PERCENT YIELD OF PCDFs AS A FUNCTION OF REACTION ATMOSPHERE

ϕ	Temperature of Maximum Yield (C)	Weight % Yield			
		Tri-CDFS	Tetra-CDFS	Penta-CDFS	Total PCDFS
0.05	750	0.66	4.3	2.0	6.9
0.2	800	0.34	1.7	0.56	2.6
1.0	900	0.13	1.3	0.25	1.7
3.0	850	0.068	0.71	0.21	0.99

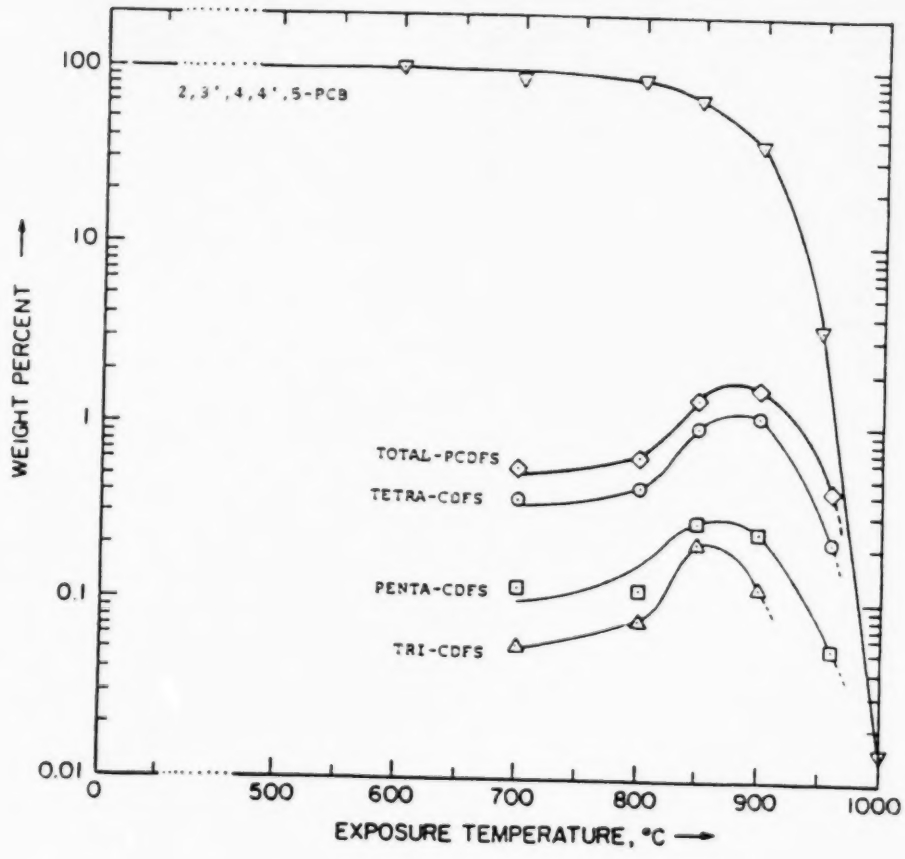
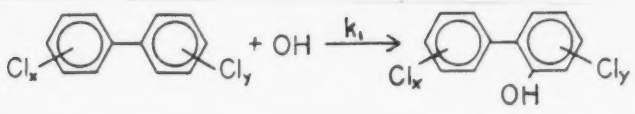
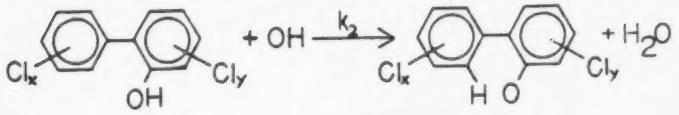


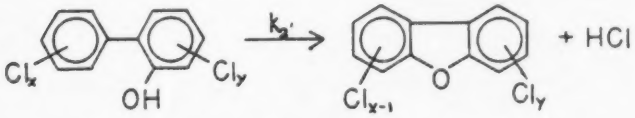
Figure 5. PCDF formation/destruction profiles for ϕ=1.0 and a gas-phase residence time of 2.0 seconds.



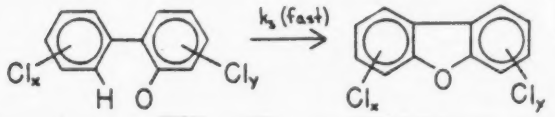
(1)



(2)



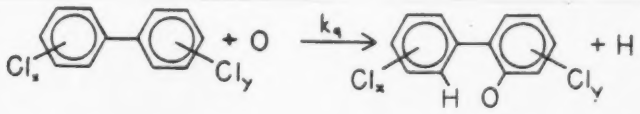
(2')



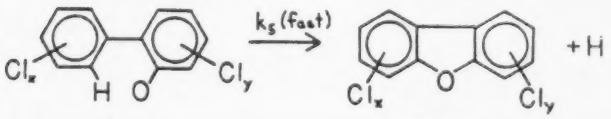
(3)

A mechanism involving reactions 1 and 2 would correspond to an HCl elimination mechanism, while as mechanisms involving reactions 1, 2, and 3, would correspond to an H_2 elimination mechanism. Reaction 1 is shown as a substitution reaction but may actually be an addition followed by H atom elimination.

Similar reaction mechanisms may be drawn for O atom attack. Reactions 4 and 5 would also result in H_2 elimination.



(4)



(5)

Reaction schemes involving Cl atom loss through addition or substitution reactions would be expected to be energetically less favorable with lower yields of PCDFs. This would account for the lower observed yields of PCDFs formed through a mechanism involving Cl_2 elimination.

The changes in yields of various products as a function of oxygen level and temperature is very important for understanding the results of PCB degradation. For example, internal arcing in a sealed capacitor would result in heating of PCBs in an oxygen-deficient environment. Under these conditions, one would predict a shift of yields towards pyrolysis products such as other PCBs, polychlorinated benzenes (PCBzs), and polynuclear aro-

matics (PNAs) rather than PCDF. However, higher temperatures are required to achieve conversion which may not be reached. On the other hand, open burning or combustion of the PCBs would occur in an environment with more available oxygen which would favor the formation of oxidative products such as PCDFs. However, even under fire conditions, oxygen-starved conditions can also exist resulting in formation of pyrolysis products.

During incineration, one would expect that oxygen-deficient combustion conditions would control the composition of the stack effluent. For thermal destruction processes that involve both flame combustion and thermal oxidation, it is contended that only the fraction of the organic waste which escapes the flame and thus undergoes degradation in an oxygen-deficient environment is responsible for most emissions. Therefore, a well-defined relationship for temperature and oxygen concentration effects on PCB degradation and product formation can be used to guide the environmentally safe incineration of PCB-containing wastes.

Formation of PICs from Chloroform

The thermal decomposition profile of chloroform and the thermal generation/decomposition profiles for two of its thermal reaction products are plotted in Figure 6. Pentachloroethane as a product is shown due to its possible role in the chloroform thermal decomposition pathway. Tetrachloroethylene is shown because of its high yields, exceptional thermal stability, and toxicity.

As shown in Figure 6, chloroform is a relatively thermally fragile compound. In a recent study by our laboratory, chloroform ranked second from the last in terms of thermal stability (1). It has also been shown to be considerably less stable than dichloromethane and carbon tetrachloride. Based on decomposition via homolysis of a C-Cl bond, chloroform would be expected to be more stable than carbon tetrachloride.

Studies by Shilov and Sabirova at temperatures ranging from 485-599C led to the conclusion that the initial step of chloroform decomposition was not simply C-Cl bond homolysis, but the direct loss of HCl to form an intermediate biradical dichlorocarbene (25). The dichlorocarbene may then further react with chloroform through insertion in the C-H bond to form pentachloroethane (26). Another proposesd reaction of dichlorocarbene is its combination with another dichlorocarbene to form tetrachloroethylene.

The thermal decomposition profile of pentachloroethane and the generation/decomposition profile for the product tetrachloroethylene are shown in Figure 7. As shown, pentachloroethane and chloroform are of comparable thermal stability. The conversion of pentachloroethane to tetrachloroethylene is very favorable and most likely occurs through the concerted elimination of HCl (27). If chloroform decomposition does proceed via the formation of pentachloroethane, then subsequent HCl elimination from the pentachloroethane would certainly contribute to the high yields of tetrachloroethylene observed.

The products identified (tentative structural assignments) from the

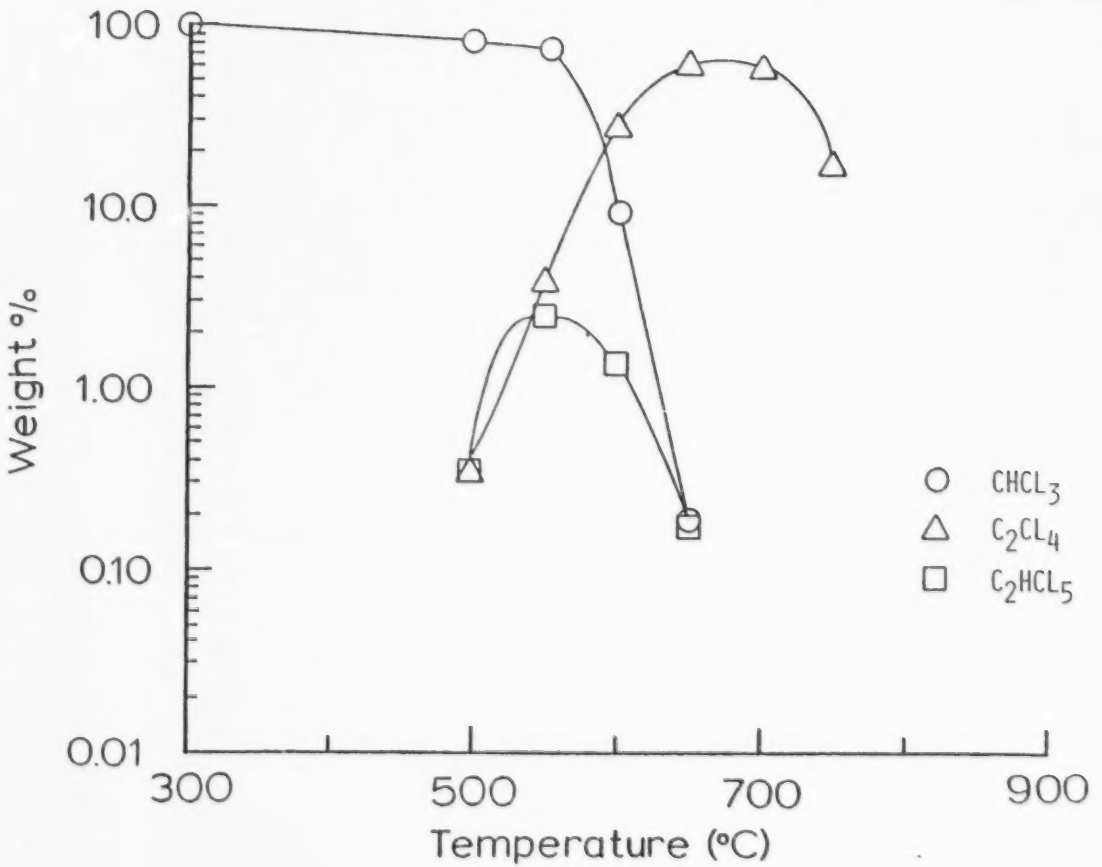


Figure 6. Weight percent (normalized to non-decomposed parent peak) vs. temperature for chloroform and selected decomposition products (ϕ = 0.76, 2.0 seconds residence time).

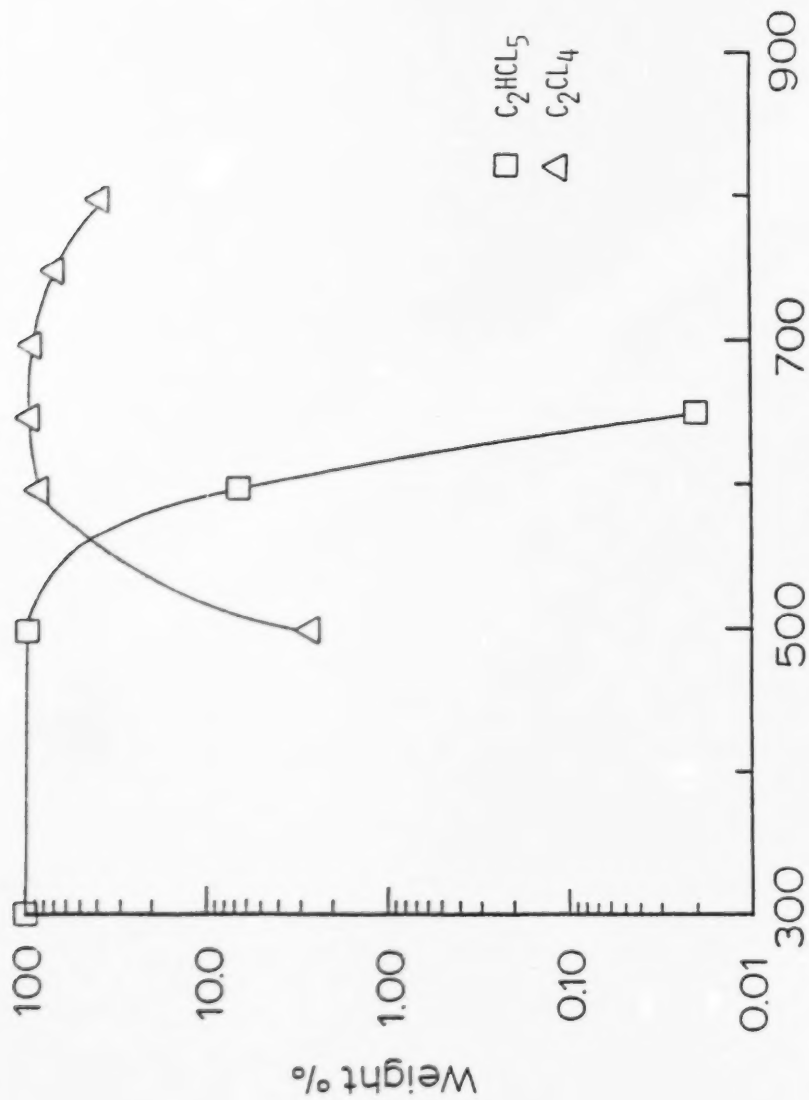


Figure 7. Weight percent (normalized to non-decomposed parent peak) vs. temperature for pentachloroethane and its major decomposition product tetrachloroethylene (ϕ = 0.76, 2.0 seconds residence time).

thermal reaction of chloroform and pentachloroethane are listed in Table 9. The similarity of the products supports the hypothesis of common decomposition pathways. Based on the observed products as well as the previously mentioned studies, decomposition pathways as shown in Figure 8 may be envisioned. Products listed in Table 9 which are not shown may be generated by further elimination of HCl and/or radical reactions.

Formation of PICs from Polychlorinated Phenols

The thermal decomposition of chlorophenols is of intense interest because of the potential formation of polychlorinated dibenzo-dioxins (PCDDs) as incomplete combustion products. Thermal decomposition data was obtained using the TDU-GC for pentachlorophenol (PCP) in nitrogen, pentachlorophenol in air, and 2,4,5-trichlorophenol (2,4,5-TCP) in nitrogen. Thermal decomposition profiles for these compounds are presented in Figure 9. The extrapolated $T_{99}(2)$ is 640C for PCP in nitrogen, 630C for PCP in air, and 775C for 2,4,5-TCP in nitrogen.

Major products of incomplete combustion were identified for PCP in nitrogen and in air using the TDAS. These partial combustion products, along with their temperatures of maximum formation, are given in Table 10.

The similarity between the thermal stability of PCP in air and nitrogen suggests that unimolecular decomposition is a significant degradation mechanism. The oxygen-hydrogen bond energy in phenol is relatively low (88 kcal/mole) and may be lower in 2,4,5-TCP and lower yet in PCP. Of course, oxygen is available in the reaction atmosphere as a degradation product of PCP and TCP, probably in the form of OH. One would expect the hydroxyl hydrogen to be susceptible to abstraction by OH. From profiling the combustion products, it was observed that all were formed at approximately equal concentrations (within a factor of 10), at their temperatures of maximum yield. It was also observed that the formation maxima for PICs generally peaked at about 630C-650C for pentachlorophenol in air and 725-775C for pentachlorophenol in nitrogen. This is interesting in light of the fact that the parent material exhibited a maximum decomposition rate between 625C and 650C in both cases. This may have occurred because in air PICs were forming directly from the parent material, while in nitrogen the principal PICs may have evolved through thermal decomposition of other PICs.

Table 10 includes only the major PICs observed at selected reaction temperatures on the TDAS. It should be noted that the production of octachlorodibenzo-p-dioxin (OCDD) was tentatively identified by retention time on the TDU-GC, and that this identification was confirmed by examining low-level peaks on the TDAS. The maximum yield in air (~1%) was observed at 500C, while the maximum yield in nitrogen (~1.5%) was seen at 550C.

Expansion of Pure Compound Kinetic and Thermal Stability Data Base

We have also generated additional pure compound thermal decomposition kinetic data. Tables 11 through 13, are a complete listing of compounds for which we have measured pseudo-first order oxidation kinetic parameters.

TABLE 9. THERMAL DECOMPOSITION PRODUCTS OBSERVED FROM:

CHLOROFORM ($CHCl_3$)	PENTACHLOROETHANE (C_2HCl_5)
	$CHCl_3$
CCl_4	CCl_4
$C_2H_4Cl_2$	$C_2H_4Cl_2$
	$C_2H_2Cl_4$
C_2HCl_3	C_2HCl_3
C_2HCl_5	
C_2Cl_2	C_2Cl_2
C_2Cl_4	C_2Cl_4
	C_2Cl_6
	$C_3H_6Cl_2$
C_3Cl_4	C_3Cl_4
	$C_4H_2Cl_6$
C_4Cl_4	
C_4Cl_6	

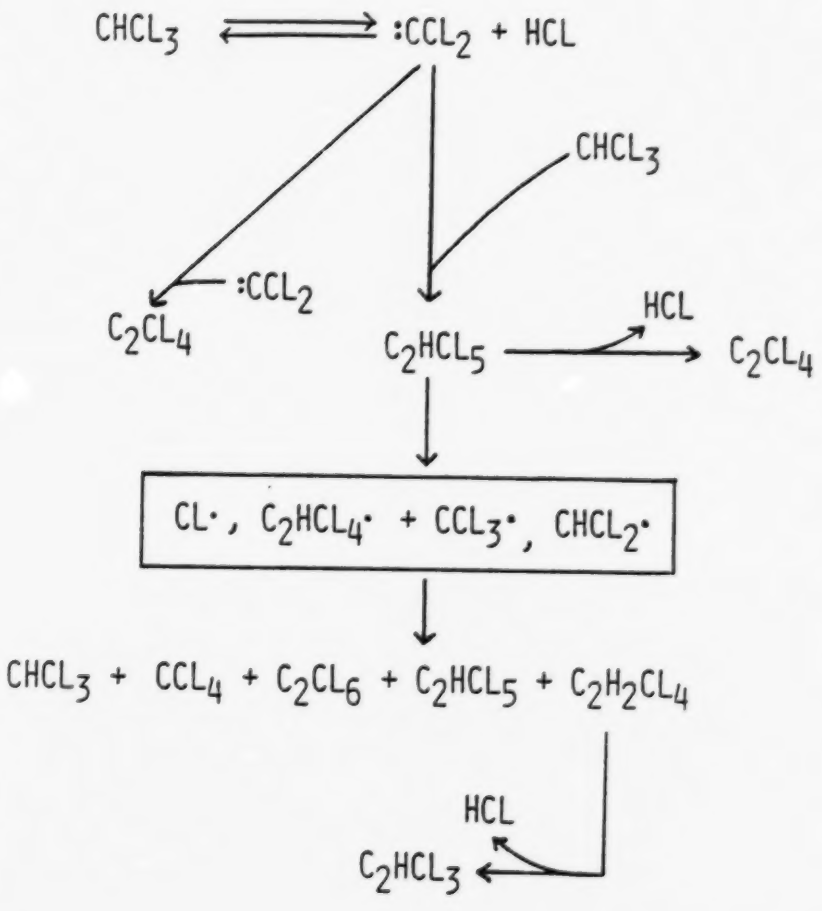


Figure 8. Possible pathways for the thermal decomposition of chloroform.

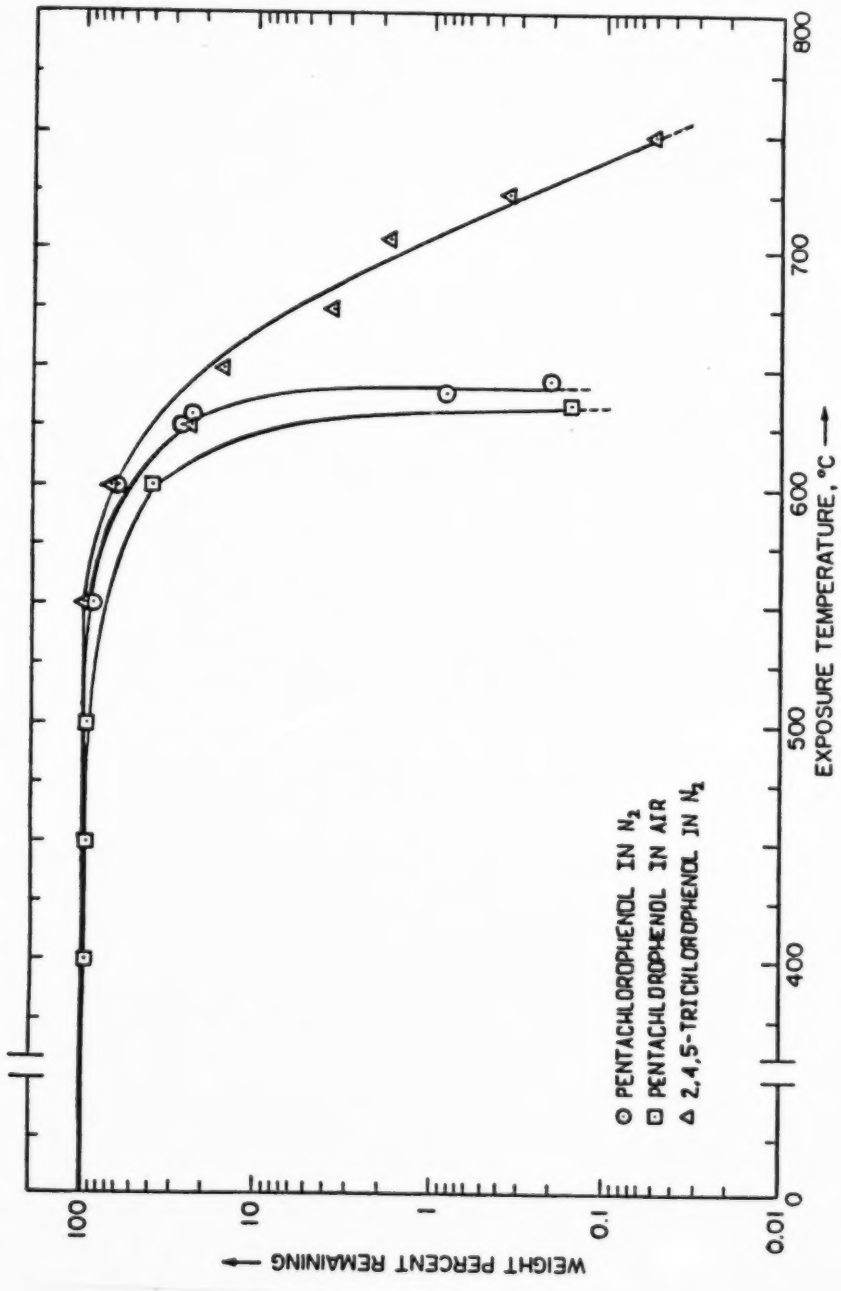


Figure 9. Thermal decomposition profiles for PCP and TCP.

TABLE 10. THERMAL DEGRADATION PRODUCTS FROM PENTACHLOROPHENOL[a]

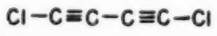
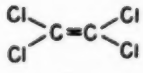
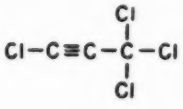
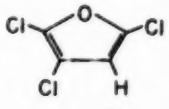
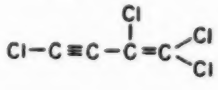
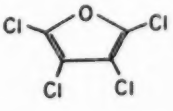
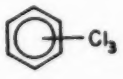
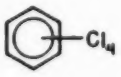
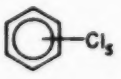
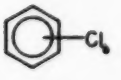
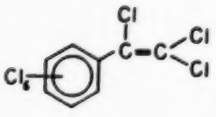
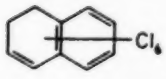
Tentative Identification	Tentative Structure	Temperature of Maximum Formation (C)	
		In N_2	In Air
Dichlorobutadiyne		800	ND[b]
Tetrachloroethylene		ND	650
Tetrachloropropyne		ND	630
Trichlorofuran		ND	630
1,1,2,4-tetrachloro-1-buten-3-yne		725	630
Tetrachlorofuran		ND	650
Trichlorobenzene		625	630
Tetrachlorobenzene		775	630
Pentachlorobenzene		725	630
Hexachlorobenzene		725	ND

TABLE 10. (Continued)

Tentative Identification	Tentative Structure	Temperature of Maximum Formation (C) In N_2	In Air
Octachlorostyrene		725	ND
Hexachlorodihydronaphthalene		725	630
Unknown chlorinated compound Molecular Weight 400		725	ND

[a]Identifications are based on mass spectra alone and are strictly tentative. Standards were not analyzed to confirm these identifications, and in some cases, library spectra were not available for comparison.

[b]ND=not detected on TDAS, with a detection limit of about 2% conversion of parent.

TABLE 11. SUMMARY OF THERMAL DECOMPOSITION DATA

Compound	Empirical Formula	T_{onset} (2) (C)	T_{99} (2) (C)	$T_{99.99}$ (2) (C)
Acetonitrile	C_2H_3N	760	900	950
Tetrachloroethylene	C_2Cl_4	660	850	920
Acrylonitrile	C_3H_3N	650	830	860
Methane	CH_4	660	830	870
Hexachlorobenzene	C_6Cl_6	650	820	880
1,2,3,4-Tetrachlorobenzene	$C_6H_2Cl_4$	660	800	850
Pyridine	C_5H_5N	620	770	840
Dichloromethane	CH_2Cl_2	650	770	780
Trichloroethylene	C_2HCl_3	600	765	935
Carbon Tetrachloride	CCl_4	600	750	820
Hexachlorobutadiene	C_4Cl_6	620	750	780
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	640	750	790
1,2-Dichlorobenzene	$C_6H_4Cl_2$	630	740	780
Ethane	C_2H_6	500	735	785
Benzene	C_6H_6	630	730	760
Aniline	C_6H_7N	620	730	750
Monochlorobenzene	C_6H_5Cl	540	710	780
Nitrobenzene	$C_6H_5NO_2$	570	670	700
Hexachloroethane	C_2Cl_6	470	600	640
Chloroform	$CHCl_3$	410	590	620
1,1,1-Trichloroethane	$C_2H_3Cl_3$	390	570	600
Triallate	$C_{10}H_{16}NSOCl_3$	360	470	525
Trifluralin	$C_{13}H_{16}N_3O_4F_3$	360	440	477

TABLE 12. SUMMARY OF FIRST ORDER KINETIC RESULTS

Compound	$A(s^{-1})$	E_a(kcal/mole)	Temperature Range	Calculated $T_{99}(2)(°C)$
Trichloroethylene	4.2×10^{3}	18	600-700	913
Acrylonitrile	1.3×10^{6}	31	750-810	910
Acetonitrile	4.7×10^{7}	40	800-850	908
Tetrachloroethylene	2.6×10^{6}	33	725-825	900
Methane	3.5×10^{9}	48	700-800	874
Hexachlorobenzene	2.5×10^{8}	41	710-785	845
1,2,3,4-Tetrachlorobenzene	1.9×10^{6}	30	700-765	834
Ethane	1.3×10^{5}	24	675-725	830
Carbon Tetrachloride	2.8×10^{5}	26	680-730	824
Monochlorobenzene	8.0×10^{4}	23	600-670	810
Dichloromethane	3.0×10^{13}	64	700-755	796
1,2,4-Trichlorobenzene	2.2×10^{8}	39	675-725	789
Pyridine	1.1×10^{5}	24	700-750	767
1,2-Dichlorobenzene	3.0×10^{8}	39	685-725	766
Hexachlorobutadiene	6.3×10^{12}	24	700-750	763
Benzene	2.8×10^{8}	38	685-715	757
Aniline	9.3×10^{15}	71	650-700	726
Nitrobenzene	1.4×10^{15}	64	600-650	672
Hexachloroethane	1.9×10^{7}	29	500-600	641
Chloroform	2.9×10^{12}	49	520-585	606
1,1,1-Trichloroethane	1.9×10^{8}	32	475-550	601
Triallate	6.8×10^{8}	31	360-460	516
Trifluralin	2.7×10^{7}	25	360-430	483

TABLE 13. SUMMARY OF FRACTIONAL REACTION ORDER CALCULATIONS

Compound	Temperature (C)	Reaction Order a	r^2
Acetonitrile	850	1.1	1.00
Acrylonitrile	810	1.6	0.98
Aniline	700	1.1	1.00
Benzene	720	1.1	0.90
Carbon Tetrachloride	730	1.5	1.00
Chloroform	585	1.1	0.98
1,2-Dichlorobenzene	725	1.3	1.00
Dichloromethane	752	0.9	0.50
Ethane	725	1.0	0.98
Hexachlorobenzene	785	0.9	1.00
Hexachlorobutadiene	730	1.0	0.99
Hexachloroethane	600	1.2	0.97
Methane	800	1.2	0.93
Monochlorobenzene	670	1.6	0.89
Nitrobenzene	650	1.1	1.00
Pyridine	750	1.3	0.99
1,2,3,4-Tetrachlorobenzene	740	1.3	0.90
Tetrachloroethylene	825	1.1	0.99
Triallate	460	1.4	0.99
1,2,4-Trichlorobenzene	725	1.4	0.99
1,1,1-Trichloroethane	550	1.2	0.96
Trichloroethylene	700	1.3	0.99
Trifluralin	430	1.3	0.99

Table 11 ranks the compounds by their experimental T_{99} (2) in an atmosphere of flowing air. Table 12 presents the E_a and A values for the compounds ranked by calculated T_{99} (2). Table 13 summarizes the calculated fractional reaction orders for the compounds, which can be used to estimate the concentration dependence of the destruction efficiency of the pure compounds. The theoretical formalism and experimental design for these studies is available from other reports to which the reader is referred for additional information (1).

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